(STOs) using the method of Bursten, Jensen, and Fenske.[31] Contracted double-ζ representations were constructed for the W 5d and O 2p, while single-ζ representations were used for all other orbitals. Valence AOs were orthogonalized to all other valence and core orbitals of the same atom. Basis functions for the W atom were derived for a +1 oxidation state with the 6s and 6p exponents fixed at 1.8. An exponent of 1.16 was used for the H 1s atomic orbital.[32]

Acknowledgment. We thank the National Science Foundation for support. D.L.C. was the Indiana University General Electric Fellow 1985–86. We thank Professors E. R. Davidson, J. J. Gajewski, L. K. Montgomery, and R. Hoffmann for stimulating discussions.

Registry No. $W_2(O\text{-}i\text{-}Pr)_6$, 71391-16-7; $W_4(O\text{-}i\text{-}Pr)_{12}$, 104911-26-4.

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Heteropolyvanadates Containing Two and Three Manganese(IV) Ions: Unusual Structural Features of $Mn_2V_{22}O_{64}{}^{10-}$ and $Mn_3V_{12}O_{40}H_3{}^{5-}$

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Abstract: The crystal structures of the vanadomanganate(IV) salts $K_{10}Mn_2V_{22}O_{64}\cdot 20H_2O$ (**1**) and $K_5H_3Mn_3V_{12}O_{40}\cdot 8H_2O$ (**2**) are reported. Compound **1** is triclinic, space group, $P\bar{1}$; a = 15.710 (4) Å, b = 12.671 (4) Å, c = 10.281 (3) Å; α = 113.62 (2)°, β = 92.56 (3)°, γ = 79.54 (3)°; Z = 1. The heteropolyanion consists of a centrosymmetric arrangement of two MnV_{11} moieties linked by two linear unsupported V–O–V bridges. Each MnV_{11} unit comprises edge-shared MO_6 octahedra and may be regarded as a manganese-substituted decavanadate structure with two additional VO_6 octahedra that contribute to the bridging section of the whole structure. The V–O bond lengths in the bridges (1.779 Å) imply bond orders of unity, and the heteropolyanion may therefore be regarded as a double "anhydride", $[(MnV_{11}O_{31})_2O_2]^{10-}$ (compare $[(C_9H_6NO)VO]_2O$ and $[(Nb_2W_4O_{18})_2O]^{2-}$). Other bond lengths and angles are unexceptional. Compound **2** is triclinic, space group, $P\bar{1}$; a = 11.800 (2) Å, b = 16.555 (2) Å, c = 11.267 (20) Å; α = 102.91 (1)°, β = 109.48 (1)°, γ = 86.88 (1)°; Z = 2. The anion is a highly condensed edge-shared C_{3v} cluster of MO_6 octahedra based on the arrangement expected for the (unknown) ϵ-isomer of the Keggin structure but with no central "tetrahedral" atom. Instead, MnO_6 octahedra occupy the centers of three of the four faces of the anion. The fourth face has an octahedral vacancy to which the three protons are attached. Although the three MnO_6 octahedra share common edges to form an equilateral triangle of Mn^{4+} cations (Mn···Mn, 2.86–2.88 Å), the anion shows virtually no magnetic coupling ($J = -0.3$ cm^{-1}) based upon susceptibility measurements to 10 K.

There is considerable current interest in the chemistry and structures of polyoxoanions of the early transition elements vanadium, molybdenum, and tungsten in view of their perceived importance in catalysts.[3] Because of the different oxidation state and stereochemical preferences of vanadium compared with molybdenum and tungsten, there is no reason to expect that the structures (or indeed the stoichiometries) of the vanadates would be similar to those of the molybdates and tungstates. However,

Table I. Crystal Data for **1**

formula	$K_{10}Mn_2V_{22}O_{64}\cdot 20H_2O$
formula wt	3005.8
crystal system	triclinic
space group	$P\bar{1}$
a, b, c (Å)	15.710 (4), 12.671 (4), 10.281 (3)
α, β, γ (deg)	113.62 (2), 92.56 (3), 79.54 (3)
cell volume	1843 (1) Å^3
Z	1
density (g·cm^{-3})	2.67 (calcd), 2.64 (obsd)
μ (Mo Kα)	3.53 mm^{-1}
$F(000)$	1358
temp	298 K
$(\sin \theta/\lambda)_{max}$	0.7035 Å^{-1}
hkl range	$-20 \le h \le 22, 0 \le k \le 17, -14 \le l \le 14$
no. reflcns	11287; 8085 ($\lvert F_o\rvert > 3.0\sigma(\lvert F_o\rvert)$)
scan mode	ω–2θ
scan speed	4° min^{-1} (ω)
$\Delta\omega$	$1.0 + 0.5 \tan \theta$
R	0.067
R_w	0.100, $w^{-1} = \sigma^2(\lvert F_o\rvert) + (0.01\lvert F_o\rvert)^2$
$(\Delta/\sigma)_{max}$	0.2
$\Delta\rho/e$ Å^{-3}	<1.8

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[2] Georgetown University.

[3] Research activity is high in this area and has not been comprehensively reviewed recently. The following lists recent papers from some different research groups (alphabetically by first author) that are currently active and provides an entree to the literature. (a) Ai, M. *Polyhedron* **1986**, *5*, 103. (b) Akid, R.; Darwent, J. R. *J. Chem. Soc., Dalton Trans.* **1986**, 395. (c) Aoshima, A.; Yamaguchi, T. *Nippon Kagaku Kaishi* **1986**, 1161. (d) Baba, T.; Ono, Y. *J. Mol. Catal.* **1986**, *37*, 317. (e) Dun, J. W.; Gulari, E.; Streusand, B. *Appl. Catal.* **1986**, *21*, 61. (f) Finkë, R. G.; Rapko, B.; Domaille, P. J. *Organometallics* **1986**, *5*, 175. (g) Fox, M. A.; Cardona, R.; Gillard, E. *J. Am. Chem. Soc.* **1987**, *109*, 6347. (h) Hill, C. L.; Brown, R. B., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 536. (i) Kulikov, S. M.; Kozhevnikov, I. I.; Fomina, M. N.; Krysin, A. P. *Izv. Acad. Nauk SSSR, Ser. Khim.* **1988**, 752. (j) Misono, M.; Okahara, T.; Ichiki, T.; Arai, T.; Kanda, Y. *J. Am. Chem. Soc.* **1987**, *109*, 5535. (k) Moffat, J. B. *Stud. Surf. Sci.* Catal. **1987**, *31*, 241. (l) Nomiya, K.; Sugie, Y.; Miyazaki, T.; Miwa M. *Polyhedron* **1986**, *5*, 1267. (m) Papaconstantinou, E.; Argitis, P.; Dimotikali, D.; Hiskia, A.; Ionnidis, A. *NATO ASI Ser., Ser. C* **1986**, *174*, 415. (n) Siedle, A. R.; Markell, C. G.; Lyon, P. A.; Hodgson, K. O.; Roe, A. L. *Inorg. Chem.* **1987**, *26*, 219. (o) Urabe, K.; Tanaka, Y.; Izumi, Y. *Chem. Lett.* **1985**, 1595. (p) Vasilevskis, J.; De Deken, J. C.; Saxton, R. J.; Wentreck, P. R.; Fellmann, J. R.; Kipnis, L. S. PCT Int. Appl. WO 01,615 [*Chem.* Abstr. **1987**, *107*, 178602p]. (q) Venturello, C.; D'Aloisio, R.; Bart, J. C. J.; Ricci, M. *J. Mol. Catal.* **1985**, *32*, 107. (r) Yamase, T.; Watanabe, R. *J. Chem. Soc., Dalton Trans.* **1986**, 1669.

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Table II. Crystal Data for **2**

formula	$K_5H_3Mn_3V_{12}O_{40}\cdot 8H_2O$
formula wt	1758.7
crystal system	triclinic
space group	$P\bar{1}$
a, b, c (Å)	11.800 (2), 16.555 (2), 11.267 (2)
α, β, γ (deg)	102.91 (1), 109.48 (1), 86.88 (1)
cell volume	2021.9 (5) $Å^3$
Z	2
density ($g\cdot cm^{-3}$)	2.90 (calcd), 2.88 (obsd)
μ (Mo $K\alpha$)	4.07 mm^{-1}
$F(000)$	1698
temp	298 K
$(\sin \theta/\lambda)_{max}$	0.6497 $Å^{-1}$
hkl range	$-15 \leq h \leq 15$, $-21 \leq k \leq 21$, $0 \leq l \leq 14$
no. reflcns	9796, 7950 ($\lvert F_o \rvert > 3.0\sigma(\lvert F_o \rvert)$)
scan mode	$\omega-2\theta$
scan speed	3° min^{-1} (ω)
$\Delta\omega$	$1.0 + 0.5 \tan \theta$
R	0.041
R_w	0.048, $w^{-1} = \sigma^2(\lvert F_o \rvert) + (0.01\lvert F_o \rvert)^2$
$(\Delta/\sigma)_{7ax}$	0.3
$\Delta\rho/e\ Å^{-3}$	<1.1

although there are, in fact, very few examples of structurally characterized heteropolyvanadates,[4] their structures do show strong similarities to the heteropolymolybdates and -tungstates. Thus the C_{2h} anion $H_2I_2V_2O_{16}^{6-}$ is isostructural with $I_2Mo_2O_{16}^{6-}$ and $I_2W_2O_{16}^{6-}$,[5] and the anions $XV_{14}O_{42}^{9-}$ (X = P, As) have D_{2d} structures[6] based on the Keggin anion $PMo_{12}O_{40}^{3-}$.

It is therefore of considerable interest to discover the structures and true compositions of the series of heteropolyvanadomaganates(IV) with Mn:V = 1:13, 1:11, and 1:4 (3:12) that were reported several years ago by Flynn and Pope[7] and which have no stoichiometric analogues in the molybdates and tungstates. The structure of the 1:13 anion was reported elsewhere,[8] for the structure of a nickel(IV) isomorph had already been described,[9] and its relationship to the mineral sherwoodite has been discussed.[10] In this paper we report the structures of the 1:11 and 1:4 complexes. The former is shown to be dimeric, $Mn_2V_{22}O_{64}^{10-}$, a possibility that had been tentatively considered earlier on rather slim evidence.[7b] The 1:4 anion has the 3:12 stoichiometry that had been proposed from analytical data and preliminary X-ray investigation.[7b]

Experimental Section

Crystallography. The crystals were prepared by the method reported earlier[7b] from a hot aqueous solution containing HNO_3, $MnSO_4$, and $K_2S_2O_8$ and were recrystallized from H_2SO_4 solution. Following isolation of red $K_{10}Mn_2V_{22}O_{64}\cdot 20H_2O$ (**1**), black parallelepipeds of $K_5H_3Mn_3V_{12}O_{40}\cdot 8H_2O$ (**2**) were deposited. Single crystals of **1** (0.1 × 0.2 × 0.3 mm) and **2** (0.25 × 0.3 × 0.3 mm) were sealed in Lindemann glass capillaries and mounted on a Rigaku automated four-circle diffractometer. Cell parameters were refined from 50 reflections in the ranges 15.3° < θ < 19.80° (**1**) and 14.5° < θ < 16.7° (**2**). Three standard reflections were monitored every 100 reflections, and other X-ray data are given in Tables I and II. The structures were solved by using Patterson functions, and all non-hydrogen atoms were located in successive Fourier syntheses. All atoms were refined with anisotropic thermal parameters by block-diagonal least squares. Final difference maps showed no peaks higher than 1.8 e $Å^{-3}$. Complex atomic scattering factors were taken from the *International Tables of X-ray Crystallography*,[11] and calculations were carried out on a HITAC M280-H computer at the Computer Center of the University of Tokyo, by using UNICS III programs.[12]

Table III. Positional and Thermal Parameters[a] for **1**

atom	x	y	z	B_{eq}
Mn	7113 (1)	2773 (1)	2387 (1)	0.85 (3)
V(1)	8805 (1)	2993 (1)	3945 (2)	1.16 (4)
V(2)	5356 (1)	2917 (2)	3819 (2)	1.46 (4)
V(3)	5597 (1)	4916 (2)	3819 (2)	1.46 (4)
V(4)	8490 (1)	560 (1)	1525 (2)	1.27 (4)
V(5)	8760 (1)	2506 (2)	682 (2)	1.27 (4)
V(6)	8496 (1)	968 (2)	4701 (2)	1.46 (4)
V(7)	8973 (1)	4966 (2)	2949 (2)	1.49 (4)
V(8)	6779 (1)	766 (1)	3087 (2)	1.39 (4)
V(9)	7273 (1)	4644 (2)	1316 (2)	1.32 (5)
V(10)	7082 (1)	3238 (1)	5609 (2)	1.12 (5)
V(11)	7321 (1)	5207 (1)	4710 (2)	1.12 (5)
K(1)	9211 (2)	−812 (2)	7323 (3)	2.3 (1)
K(2)	4052 (4)	7023 (4)	1268 (5)	6.3 (1)
K(3)	6385 (3)	6680 (3)	8891 (4)	3.9 (1)
K(4)	9786 (3)	7828 (3)	2756 (4)	4.2 (2)
K(5)	3610 (4)	603 (4)	3361 (7)	6.8 (2)
Oa(1)	7769 (4)	2037 (5)	3478 (7)	1.0 (2)
Oa(2)	7980 (4)	3723 (6)	2729 (7)	1.0 (2)
Ob	6549 (4)	3915 (6)	4128 (7)	1.0 (2)
Oc(1)	7808 (4)	1674 (6)	785 (7)	1.0 (2)
Oc(2)	6257 (4)	1869 (6)	2252 (7)	1.1 (2)
Oc(3)	6491 (5)	3649 (6)	1441 (7)	1.2 (2)
Oc(4)	9180 (4)	1844 (6)	2071 (7)	1.2 (2)
Oc(5)	7964 (4)	4078 (6)	5414 (7)	1.1 (2)
Oc(6)	6264 (5)	2184 (6)	4782 (7)	1.4 (2)
Oc(7)	6681 (4)	5568 (6)	3252 (7)	1.2 (2)
Od(1)	8998 (5)	139 (6)	2918 (8)	1.5 (2)
Od(2)	9425 (5)	3618 (7)	1377 (8)	1.6 (2)
Od(3)	9243 (5)	2180 (6)	4853 (7)	1.4 (2)
Od(4)	9442 (5)	3951 (7)	4053 (7)	1.5 (2)
Od(5)	7508 (5)	−43 (6)	1541 (8)	1.5 (2)
Od(6)	7944 (5)	3413 (6)	5 (7)	1.4 (2)
Od(7)	7542 (5)	294 (6)	4259 (8)	1.7 (2)
Od(8)	8180 (5)	5483 (6)	1938 (8)	1.6 (2)
Od(9)	7803 (5)	2295 (6)	6169 (7)	1.4 (2)
Od(10)	8233 (5)	5798 (6)	4628 (7)	1.5 (2)
Od(11)	5036 (4)	3740 (6)	2736 (8)	1.4 (2)
Od(12)	4888 (5)	4008 (7)	5476 (8)	1.6 (2)
Oe(1)	8988 (5)	−377 (7)	110 (8)	2.0 (2)
Oe(2)	9257 (5)	1579 (7)	−754 (8)	1.8 (2)
Oe(3)	9060 (5)	369 (7)	5632 (9)	2.2 (2)
Oe(4)	9686 (6)	5755 (8)	3204 (9)	2.4 (2)
Oe(5)	6057 (6)	−23 (7)	2824 (10)	2.2 (2)
Oe(6)	6728 (5)	5277 (7)	403 (8)	2.0 (2)
Oe(7)	6598 (5)	4185 (7)	7045 (8)	1.9 (2)
Oe(8)	6831 (5)	6144 (7)	6131 (8)	1.8 (3)
Oe(9)	4704 (5)	2010 (7)	3379 (10)	2.2 (2)
Oe(10)	5144 (6)	5361 (8)	1746 (9)	2.3 (3)
Aq(1)	5404 (8)	1331 (12)	6377 (12)	4.3 (3)
Aq(2)	8729 (9)	7161 (11)	7432 (14)	4.9 (4)
Aq(3)	8291 (9)	8183 (10)	4857 (16)	5.4 (4)
Aq(4)	3608 (8)	2075 (9)	6268 (14)	4.4 (5)
Aq(5)	8773 (9)	4175 (14)	8266 (12)	5.5 (4)
Aq(6)	9246 (11)	6275 (15)	185 (14)	7.4 (5)
Aq(7)	7122 (12)	8530 (13)	8667 (15)	6.5 (5)
Aq(8)	7439 (10)	7630 (11)	1352 (16)	5.7 (6)
Aq(9)	2591 (7)	9023 (10)	2098 (10)	3.5 (6)
Aq(10)	4523 (28)	9429 (43)	287 (36)	10.5 (15)
Aq(11)	4902 (28)	8397 (32)	354 (32)	9.1 (19)

[a] Positional parameters are multiplied by 10 000. $B_{eq} = {}^4/_3 * a^*(\beta)^* a$.

Magnetic Measurements. Susceptibility data for **2** were acquired on a SQUID magnetometer at the University of Virginia.[13] The field strength was 0.5 T, and the temperature range was 10–300 K. A diamagnetic correlation of -505.9×10^{-6} was calculated.

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Table VI. Selected Bond Lengths for $Mn_2V_{22}O_{64}^{10-}$

Mn	–Oa1	1.891 (8)	V-6	–Oa1	2.323 (8)
	–Oa2	1.907 (8)		–Od1	1.836 (7)
	–Ob	1.919 (6)		–Od3	2.052 (9)
	–Oc1	1.912 (6)		–Od7	1.810 (9)
	–Oc2	1.885 (8)		–Od9	1.934 (6)
	–Oc3	1.877 (8)		–Oe3	1.593 (10)
V-1	–Oa1	2.127 (8)	V-8	–Oa1	2.347 (8)
	–Oa2	2.108 (8)		–Oc2	1.961 (8)
	–Oc4	1.929 (6)		–Oc6	2.003 (6)
	–Oc5	1.941 (6)		–Od5	1.822 (7)
	–Od3	1.619 (9)		–Od7	1.854 (9)
	–Od4	1.676 (9)		–Oe5	1.589 (10)
V-2	–Ob	2.386 (8)	V-10	–Oa1	2.286 (6)
	–Oc2	2.042 (6)		–Ob	2.104 (8)
	–Oc6	2.001 (8)		–Oc5	1.956 (8)
	–Od11	1.808 (9)		–Oc6	1.943 (8)
	–Od12	1.792 (7)		–Od9	1.744 (8)
	–Oe9	1.596 (9)		–Oe7	1.596 (7)
V-4	–Oa1	2.289 (6)			
	–Oc1	1.990 (8)			
	–Oc4	1.999 (8)			
	–Od1	1.824 (9)			
	–Od5	1.845 (9)			
	–Oe1	1.586 (7)			

Results and Discussion

Potassium 22-Vanadodimanganate(IV). Atomic and thermal parameters are listed in Table III and selected bond lengths in Table VI. The anion comprises two $MnV_{11}O_{34}$ clusters of edge-shared VO_6 octahedra linked by fusion at two vertices to yield a structure of nominal C_{2h} symmetry, see Figure 1. Each half-unit may be dissected to reveal other familar polyoxoanion structures, i.e., planar MnV_6O_{24} ("Anderson") or MnV_9O_{28} (Mn-substituted "decavanadate").[4] With the exception of the two vanadium atoms (denoted V-1) that, together with the manganese atoms, lie on the anion's mirror plane, each vanadium is bound to one terminal oxygen (Oe) and occupies a site of nominal C_{4v} local symmetry. The V–O bond length ranges are 1.580–1.597 Å (Oe); 2.273–2.428 Å (O trans to Oe); and 1.744–2.104 Å (bridging O—the longer bonds involving more highly coordinated oxygens). Coordination around V-1 resembles that for the corresponding vanadium in the decavanadate anion;[14] the two μ_2-oxygens (Od3, Od4) can be considered as quasi-terminal with V–O = 1.692, 1.676 Å (compare with 1.69 Å for the corresponding bonds in decavanadate and 1.65 Å for true V–O (terminal) bonds in *cis*-$VO_2(C_2O_4)_2^{3-}$). The two halves of the anion are linked by almost linear V–O–V bridges (178.9°) with V–O = 1.792–1.780 Å; this feature is discussed below.

As expected for a d^3 cation the coordination of the Mn atoms is quite regular (Mn–O = 1.877–1.979 Å). There is however a displacement of the Mn towards the exposed face of the MnO_6 octahedron as revealed by OMnO angles of 95.5–97.3° compared with angles of 87.2–87.7° on the opposite side of the octahedron. Such a displacement is rationalized by considerations of metal cation repulsions as for other condensed structures. Remarkably for a polyoxometalate structure all the potassium counterions could be unambiguously located. The coordination spheres of the potassium cations (see Table VII) comprise the hydrate water molecules (all of which are accounted for in this way) and surface oxygen atoms of the anions, most commonly the Oe atoms. The results of bond length–bond strength calculations using the equation[15]

$$S_{\text{x-o}} = (d_{\text{x-o}}/R^{\circ})^{-n} \tag{1}$$

are given in Table VIII. The sums of the bond strengths around each atom are unexceptional and correspond to the valence states as expected.

Table VII. Potassium Coordination Spheres in **1**

K(1)	–Oe1	2.719 (9)	K(2)	–Oe10	2.657 (11)
	–Oe2	2.891 (7)		–Aq9	2.958 (12)
	–Oe3	2.690 (12)		–Aq11	2.822 (48)
	–Aq2	2.852 (16)		–Oc3	2.713 (9)
	–Aq3	2.809 (14)		–Od6	3.397 (9)
	–Oc4	2.793 (7)		–Oe6	3.170 (10)
	–Od1	3.132 (9)		–Oe7	3.041 (12)
	–Aq9	3.200 (11)		–Aq1	2.712 (12)
K(3)	–Oe6	2.767 (11)	K(4)	–Od1	2.906 (9)
	–Oe7	2.928 (8)		–Oe4	2.874 (12)
	–Oe8	2.733 (9)		–Aq3	3.110 (16)
	–Aq7	2.886 (20)		–Aq6	2.796 (14)
	–Aq8	2.916 (15)		–Od3	2.837 (9)
	–Aq11	2.876 (36)		–Oe2	2.998 (11)
	–Od11	2.730 (8)		–Oe3	3.075 (10)
				–Aq5	2.943 (14)
K(5)	–Oe9	2.687 (12)			
	–Aq4	2.819 (13)			
	–Aq9	2.674 (13)			
	–Aq10	3.181 (36)			
	–Aq1	2.755 (15)			
	–Aq3	3.347 (15)			
	–Aq7	2.835 (19)			

Table VIII. Bond Strength Sums for Atoms in **1**

Mn	4.07	V1	5.02	V2	5.08	V3	5.13	V4	5.10
V5	5.09	V6	5.12	V7	5.15	V8	5.07	V9	5.08
V10	4.98	V11	5.05	Oa1	2.12	Oa2	2.11	Ob	1.93
Oc1	1.85	Oc2	1.88	Oc3	1.89	Oc4	1.95	Oc5	2.01
Oc6	1.85	Oc7	1.88	Od1	1.86	Od2	1.84	Od3	1.86
Od4	1.91	Od5	1.84	Od6	1.88	Od7	1.85	Od8	1.88
Od9	1.88	Od10	1.86	Od11	1.95	Od12	2.10	Oe1	1.80
Oe2	1.75	Oe3	1.76	Oe4	1.83	Oe5	1.78	Oe6	1.76
Oe7	1.75	Oe8	1.80	Oe9	1.75	Oe10	1.79		

The polyanion has two unusual structural features: (1) an unsupported linear M–O–M bridge and (2) a *staggered* configuration of the terminal M═O bonds in a linear M(O)–O–M(O) moiety, which has previously been observed only in a pinacolate complex of Mo(VI)[16] and in the present case is imposed by the constraints of the double M–O–M bridge.

The linear M–O–M bridge is only the second example of such an arrangement for six-coordinate vanadium(V), although several are known for molybdenum(VI).[17] The other vanadium case was reported in 1984 for [(oxine)VO]$_2$O, **3**, oxine = 8-hydroxyquinolinate anion)[18] which has V–O(V) = 1.779 Å and a bridge angle of 173.4°. The bond lengths in both complex **3** and the polyvanadate are consistent with a bond order of one, and Floriani et al. have shown that I behaves as an analogue of an organic anhydride and may be esterified, acylated, and base-hydrolyzed to a monomeric product.[19] Precedents exist for similar chemistry with isopolyanions of molybdenum[20] and niobium,[21] and we are investigating the possible analogous reactivity of the vanadomanganate anion.

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(14) Evans, H. T., Jr. *Inorg. Chem.* **1966**, *5*, 967.

(15) Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985**, *B41*, 244.

(16) (a) Matheson, A. J.; Penfold, B. R. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2707. (b) Other *yellow* diolato complexes of Mo(VI) probably have analogous structures, see: Knobler, C.; Penfold, B. R.; Robinson, W. T.; Wilkins, C. J.; Yong, S. H. *J. Chem. Soc., Dalton Trans.* **1980**, 248.

(17) Stiefel, E. I. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. 3, pp 1408–1412.

(18) Yamada, S.; Katayama, C.; Tanaka, J.; Tanaka, M. *Inorg. Chem.* **1984**, *23*, 253.

(19) Giacomelli, A.; Floriani, C.; Duarte, A. O.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1982**, *21*, 3310.

(20) Although they have not been directly interconverted, the polymolybdate species $(Mo_8O_{27}^{6-})_\infty$ [Böschen, F.; Buss, B.; Krebs, B. *Acta Crystallogr., Sect. B* **1974**, *B30*, 48], $Mo_8O_{26}(OH)_2^{6-}$ [Isobe, M.; Marumo, F.; Yamase, T.; Ikawa, T. *Acta Crystallogr., Sect. B* **1978**, *B34*, 2728], and $Mo_8O_{26}(OCH)_2^{6-}$ [Adams, R. S.; Klemperer, W. G.; Liu, R. S. *J. Chem. Soc., Chem. Commun.* **1979**, 256] may be considered to be "anhydride", "acid", and "formyl ester", respectively.

(21) See the reactions of $(Nb_2W_4O_{18})_2O^{6-}$ and $Nb_2W_4O_{19}H^{3-}$ [Day, V. W.; Klemperer, W. G.; Schwartz, C. *J. Am. Chem. Soc.* **1987**, *109*, 6030].

Table IX. Positional and Thermal Parameters for **2**

atom	*x*	*y*	*z*	B_{eq}
Mn(1)	95042 (6)	19931 (4)	80758 (6)	0.93 (2)
Mn(2)	74804 (6)	26297 (4)	63301 (6)	0.99 (2)
Mn(3)	74301 (6)	24814 (4)	88102 (6)	0.97 (2)
V(1)	79914 (7)	7352 (5)	55867 (8)	1.44 (2)
V(2)	57035 (7)	12918 (5)	63844 (8)	1.47 (2)
V(3)	79551 (7)	5826 (5)	83103 (8)	1.36 (2)
V(4)	96151 (7)	20276 (5)	54163 (7)	1.29 (2)
V(5)	51792 (7)	31064 (5)	69663 (8)	1.41 (2)
V(6)	95341 (7)	17477 (5)	106801 (7)	1.29 (2)
V(7)	112761 (7)	32112 (5)	78730 (7)	1.33 (2)
V(8)	90606 (7)	39271 (5)	59978 (7)	1.37 (2)
V(9)	67936 (7)	44857 (5)	67581 (8)	1.51 (2)
V(10)	67655 (7)	42983 (5)	94422 (7)	1.31 (2)
V(11)	89410 (7)	36199 (5)	113152 (7)	1.27 (2)
V(12)	112500 (7)	30820 (5)	105608 (7)	1.26 (2)
K(1)	53891 (10)	62549 (7)	93622 (11)	2.18 (3)
K(2)	89292 (10)	98864 (7)	22967 (11)	2.13 (3)
K(3)	72911 (10)	55092 (7)	35349 (12)	2.48 (3)
K(4)	65915 (12)	86416 (9)	92930 (14)	3.35 (4)
K(5)	78698 (12)	83309 (9)	59081 (16)	3.83 (5)
Oa	7780 (2)	1778 (2)	7348 (3)	1.1 (1)
Ob(1)	9173 (3)	2821 (2)	7096 (3)	1.2 (1)
Ob(2)	7180 (3)	3304 (2)	7810 (3)	1.1 (1)
Ob(3)	9126 (3)	2698 (2)	9466 (3)	1.2 (1)
Oc(1)	9607 (3)	1263 (2)	6557 (3)	1.3 (1)
Oc(2)	7858 (3)	1824 (2)	5041 (3)	1.2 (1)
Oc(3)	5827 (3)	2314 (2)	5763 (3)	1.3 (1)
Oc(4)	5787 (3)	2194 (2)	7913 (3)	1.4 (1)
Oc(5)	7791 (3)	1566 (2)	9623 (3)	1.2 (1)
Oc(6)	9583 (3)	1132 (2)	8964 (3)	1.2 (1)
Oc(7)	11085 (3)	2374 (2)	8831 (3)	1.2 (1)
Oc(8)	7370 (3)	3558 (2)	5649 (3)	1.3 (1)
Oc(9)	7275 (3)	3297 (2)	10160 (3)	1.2 (1)
Odp(1)	10845 (3)	3867 (2)	9377 (3)	1.5 (1)
Odp(2)	8591 (3)	4580 (2)	7485 (3)	1.5 (1)
Odp(3)	8581 (3)	4423 (2)	10110 (3)	1.4 (1)
Od(1)	8240 (3)	121 (2)	6805 (3)	1.5 (1)
Od(2)	6366 (3)	734 (2)	5203 (3)	1.7 (1)
Od(3)	6332 (3)	605 (2)	7485 (3)	1.6 (1)
Od(4)	11126 (3)	2375 (2)	6455 (3)	1.3 (1)
Od(5)	9260 (3)	3000 (2)	4865 (3)	1.3 (1)
Od(6)	5343 (3)	3948 (2)	6228 (3)	1.7 (1)
Od(7)	5305 (3)	3818 (2)	8514 (3)	1.5 (1)
Od(8)	9123 (3)	2634 (2)	11772 (3)	1.4 (1)
Od(9)	11060 (3)	2159 (2)	11089 (3)	1.4 (1)
Od(10)	10657 (3)	3995 (2)	6978 (3)	1.4 (1)
Od(11)	6699 (3)	4964 (2)	8344 (3)	1.5 (1)
Od(12)	10573 (3)	3775 (2)	11619 (3)	1.4 (1)
Oe(1)	8214 (3)	100 (2)	4399 (3)	2.3 (1)
Oe(2)	4296 (3)	1073 (2)	5773 (4)	2.4 (1)
Oe(3)	8115 (3)	−161 (2)	9035 (3)	2.1 (1)
Oe(4)	9827 (3)	1382 (2)	4214 (3)	1.9 (1)
Oe(5)	3780 (3)	2863 (2)	6330 (3)	2.2 (1)
Oe(6)	9731 (3)	1020 (2)	11446 (3)	2.1 (1)
Oe(7)	12691 (3)	3389 (2)	8399 (3)	2.1 (1)
Oe(8)	8893 (3)	4630 (2)	5210 (3)	2.2 (1)
Oe(9)	6520 (3)	5204 (2)	5990 (4)	2.4 (1)
Oe(10)	6486 (3)	4892 (2)	10637 (3)	1.9 (1)
Oe(11)	8681 (3)	4226 (2)	12500 (3)	2.1 (1)
Oe(12)	12665 (3)	3236 (2)	11202 (3)	2.1 (1)
Aq(1)	8601 (3)	6676 (2)	5787 (3)	2.6 (1)
Aq(2)	5200 (4)	2088 (3)	303 (4)	3.3 (1)
Aq(3)	7041 (4)	8749 (3)	2022 (4)	3.5 (1)
Aq(4)	5265 (4)	521 (3)	2408 (4)	3.8 (1)
Aq(5)	6660 (4)	294 (3)	767 (4)	3.8 (2)
Aq(6)	3917 (4)	2313 (3)	3310 (4)	4.5 (2)
Aq(7)	7109 (4)	2360 (4)	2581 (4)	5.4 (2)
Aq(8)	5903 (5)	4038 (3)	3148 (5)	5.5 (2)

[a] Positional parameters are multiplied by 100 000 for Mn, V and K and by 10 000 for the others. $B_{eq} = {}^4/_3 {}^* a^* (\beta)^* a$.

As reported earlier[7b] the potassium salt may be recrystallized from solutions of pH 2–3, but at higher pH (potassium acetate–acetic acid buffer) considerable quantities of $K_7MnV_{13}O_{38}$ were produced. At pH 3.0 mixtures of 2:22 and 1:13 complexes were recovered. Conversely, treatment of $K_7MnV_{13}O_{38}$ with bisulfate/sulfate led to virtual quantitative conversion to the 2:22 complex according to the equation

Table XII. Selected Bond Length Ranges, Assuming C_{3v} Symmetry

Mn(1)	-Oa	1.943 (2)–1.956 (4)
	-Ob1,3	1.892 (4)–1.916 (4)
	-Oc1,5	1.894 (3)–1.902 (4)
	-Oc7	1.846 (4)–1.852 (3)
V(1)	-Oe1	1.593 (4)–1.609 (3)
	-Oa	2.394 (3)–2.429 (4)
	-Oc1,2	1.989 (3)–2.013 (4)
	-Od1,2	1.817 (4)–1.831 (3)
V(4)	-Oe4	1.597 (4)–1.609 (3)
	-Ob1	2.240 (4)–2.248 (4)
	-Oc1,2	1.983 (4)–2.006 (4)
	-Od4,5	1.816 (3)–1.848 (3)
V(7)	-Oe7	1.581 (4)–1.599 (4)
	-Ob1	2.343 (3)–2.443 (3)
	-Oc7	1.982 (4)–2.002 (4)
	-Od4	1.800 (4)–1.830 (3)
	-Od10	1.796 (4)–1.862 (4)
	-Odp1	1.995 (4)–2.038 (4)

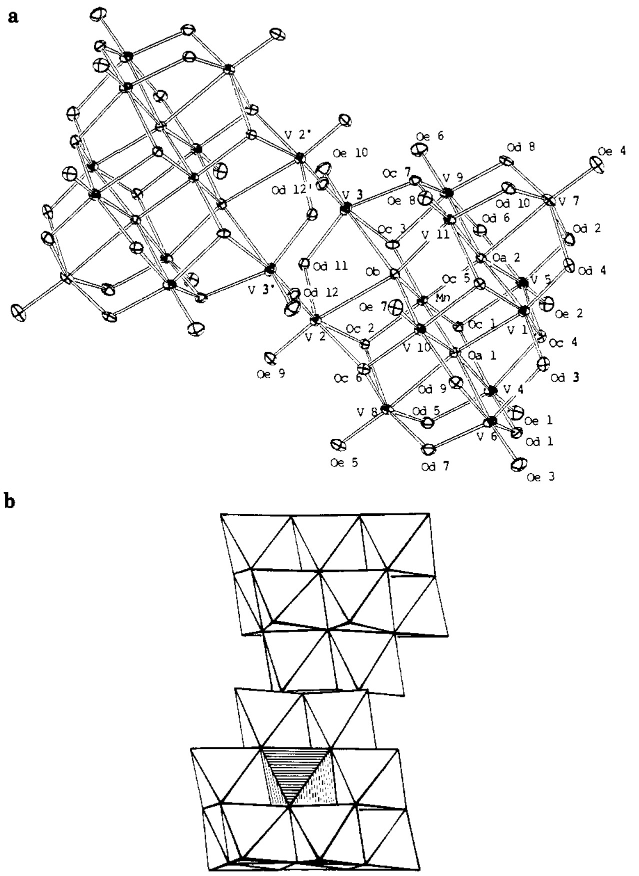

Figure 1. Representations of the structure of $Mn_2V_{22}O_{64}{}^{10-}$ from the same perspective: (a) ORTEP view, showing atom-labeling scheme and (b) polyhedral representation, one MnO_6 octahedron shown shaded. The second MnO_6 octahedron is concealed by the other half-anion.

$$2MnV_{13}O_{38}{}^{7-} + 4H^+ \rightarrow Mn_2V_{22}O_{64}{}^{10-} + 2V_2O_5 + 2H_2O$$

Although we may speculate that the Mn_2V_{22} anion is formed by condensation of two $MnV_{11}O_{31}(OH)_2{}^{5-}$ or $MnV_{11}O_{32}(OH_2)^{5-}$ moieties,[22] there is no obvious unambiguous route to such an MnV_{11} unit from MnV_{13}.[23] However, we note that by virtue of

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(22) Compare $2[PMo_9O_{31}(OH_2)_3]^{3-} \rightarrow [P_2Mo_{18}O_{62}]^{6-} + 6H_2O$ see ref 4a, p 74.

(23) Eleven-twelfths of the desired twelve-octahedron structure is obtained by removal of a trigonal edge-shared group of VO_6 octahedra from $MnV_{13}O_{38}{}^{7-}$.

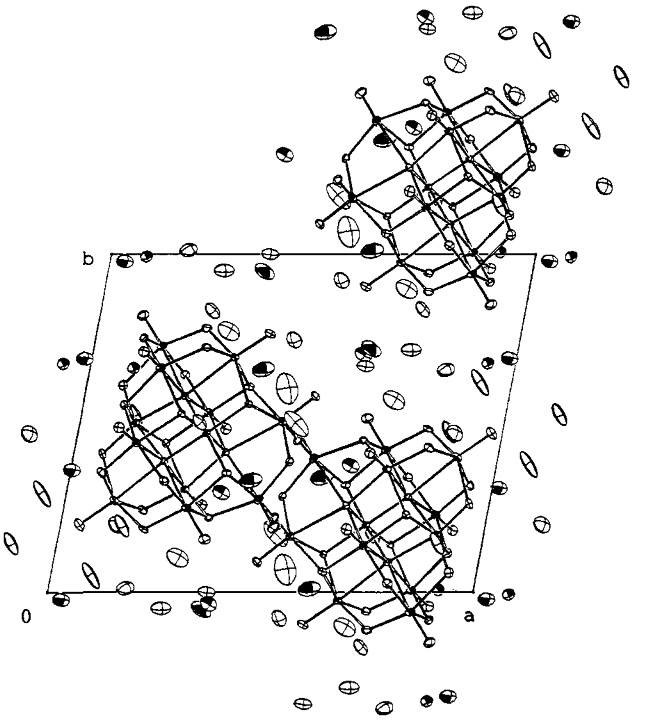

Figure 2. Unit cell contents of $K_{10}Mn_2V_{22}O_{64}\cdot20H_2O$ projected along *c* Supplementary Material.

Table XIII. Potassium Coordination Spheres in **2**

K(1)	–Oc9	3.379 (4)	K(2)	–Oe1	2.715 (4)
	–Od7	2.803 (4)		–Oe4	2.879 (3)
	–Oe7	2.741 (3)		–Oe6	2.635 (4)
	–Oe10	2.993 (4)		–Aq3	2.888 (5)
	–Oe12	2.795 (4)		–Oc1	2.743 (4)
	–Aq2	2.767 (5)		–Oc6	2.866 (4)
	–Aq8	2.674 (5)		–Od1	3.151 (4)
K(3)	–Oe8	2.793 (4)	K(4)	–Oe3	2.870 (4)
	–Oe9	3.330 (5)		–Aq3	2.906 (5)
	–Aq1	2.842 (3)		–Od9	3.124 (4)
	–Od6	3.268 (4)		–Oe12	3.162 (4)
	–Od10	2.869 (4)		–Aq2	2.703 (6)
	–Oe5	2.908 (4)		–Aq4	2.907 (5)
	–Oe7	3.145 (5)		–Aq6	2.884 (4)
K(5)	–Od1	2.916 (4)			
	–Od4	3.228 (4)			
	–Oe2	2.903 (4)			
	–Oe4	2.837 (4)			
	–Oe5	2.996 (3)			
	–Oe6	3.366 (3)			
	–Aq6	2.875 (6)			

its dimeric structure no VO_6 octahedron in Mn_2V_{22} has more than one unshared oxygen (type I[24]), whereas the MnV_{13} anion (and the MnV_{11} "monomer") have structures that contain octahedra with two terminal oxygens (type II). Such structures are in this sense less condensed than that of Mn_2V_{22}, and their conversion to the latter in acidic media is therefore understandable. Analogous reactions are observed in heteropolytungstate and -molybdate chemistry, e.g., $PW_{11}O_{39}^{7-}$ which contains type II WO_6 octahedra is converted to type I $PW_{12}O_{40}^{3-}$ upon acidification.

Potassium 12-Vanado-3-manganate(IV). Atomic and thermal parameters are listed in Table IX and selected bond lengths in Table XII. The compact structure of virtual C_{3v} symmetry (Figure 3) can be described in several ways. The twelve VO_6 octahedra form an "ε-isomer"[25] of a Keggin structure that lacks a central tetrahedron. The resulting structure has four tetrahedrally related "faces" comprising rings of six edge-shared VO_6 octahedra. Manganese atoms occupy octahedral cavities in the centers of three of the four faces. As a result the three Mn atoms occupy a trigonal Mn_3O_{13} unit (comprising edge-shared MnO_6 octahedra) at the center of the anion. Upon the basis of manganese oxidation state determination,[7b] the anion oxygen count, and cation analysis (five K^+ per anion) the anion is triply protonated. All five cations were located; their coordination spheres occupied by water molecules and surface oxygens of the anion (Table XIII). The three protons can be located with a high degree of confidence on the doubly bridging oxygens (Odp1–3) that ring the octahedral cavity in the center of the manganese-deficient face of the anion. Bond lengths to these oxygens (1.995–2.038 Å) are significantly longer than for other doubly bridging oxygens (1.796–1.862 Å) and lead to valence sums for Odp1–3 (using eq

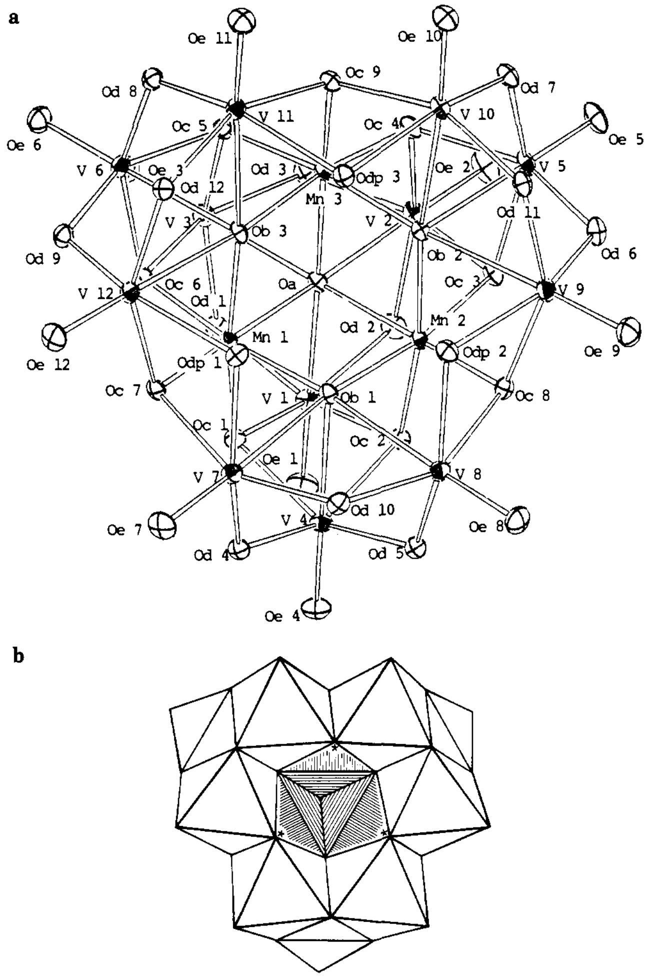

Figure 3. Representations of the structure of $H_3Mn_3V_{12}O_{40}^{5-}$ viewed along the virtual C_3 axis: (a) ORTEP view, showing atom-labeling scheme and (b) polyhedral representation with MnO_6 octahedra shown shaded. An additional edge-shard group of three VO_6 octahedra that completes an $Mn_3V_3O_{19}$ cluster is not visible from the perspective shown. Protonation sites are identified with asterisks.

Table XIV. Bond Strength Sums for Atoms in **2**

Mn1	4.07	Mn2	4.01	Mn3	4.04	V1	5.04	V2	5.04
V3	5.00	V4	5.02	V5	5.09	V6	5.02	V7	5.07
V8	5.04	V9	5.07	V10	5.09	V11	5.02	V12	5.09
Oa	2.34	Ob1	2.04	Ob2	2.01	Ob3	2.03	Oc1	1.87
Oc2	1.83	Oc3	1.87	Oc4	1.87	Oc5	1.86	Oc6	1.86
Oc7	1.95	Oc8	1.96	Oc9	2.00	Od1	1.88	Od2	1.92
Od3	1.89	Od4	1.86	Od5	1.87	Od6	1.87	Od7	1.89
Od8	1.90	Od9	1.91	Od10	1.94	Od11	1.92	Od12	1.82
Odp1	1.18	Odp2	1.16	Odp3	1.08	Oe1	1.76	Oe2	1.74
Oe3	1.76	Oe4	1.69	Oe5	1.74	Oe6	1.75	Oe7	1.76
Oe8	1.82	Oe9	1.83	Oe10	1.74	Oe11	1.79	Oe12	1.77

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[24] Pope, M. T. *Inorg. Chem.* **1972**, *11*, 1973.

[25] This isomer is produced by π/3 rotation of each of the four edge-shared M_3O_{13} groups of the Keggin structure, see ref 4a, p 27. The ε-structure has been observed previously for $[Al_{13}O_4(OH)_{24}(OH_2)_{12}]^{7+}$ [Johansson, G. *Arkiv Kemi* **1963**, *20*, 305, 321].

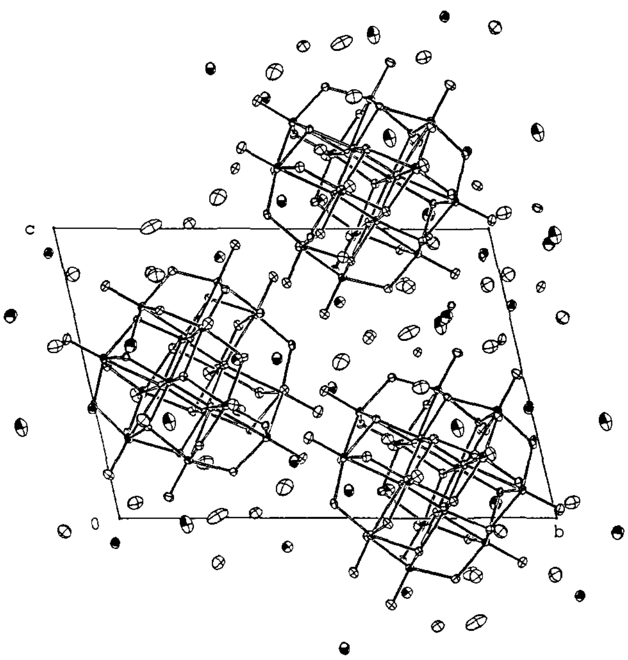

Figure 4. Unit cell contents of $K_5H_3Mn_3V_{12}O_{40}\cdot 8H_2O$ projected along *a* (Supplementary Material).

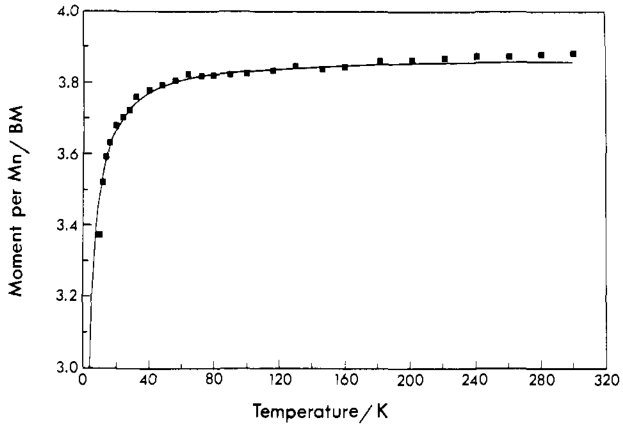

Figure 5. Temperature dependence of the magnetic moment per manganese ion for $K_5H_3Mn_3V_{12}O_{40}\cdot 8H_2O$. The line is drawn for $J = -0.3$ cm^{-1}, using the equation cited in the text.

1 of 1.08–1.18 in contrast to those for all other oxygen atoms in the anion (1.74–2.34), see Table XIV. The question arises as to why a fourth manganese atom is not incorporated, to yield the structure of T_d symmetry, $Mn_4V_{12}O_{40}{}^{4-}$: there is no satisfactory answer other than invoking an overall increase in cation–cation repulsions. As in the Mn_2V_{22} anion, bond angles around the Mn atoms demonstrate displacement along a pseudo-trigonal axis from the centers of their respective MnO_6 octahedra toward the exterior of the anion. The three MnO_6 octahedra, with three adjacent VO_6 octahedra (containing V-1, V-2, and V-3), form an M_6O_{19} octahedral cluster of edge-shared octahedra. The Mn···Mn distances are 2.857, 2.864, and 2.879 Å and are significantly shorter than the corresponding V···V separations of 3.149, 3.150, and 3.178 Å. The formally six-coordinate oxygen in the center of this cluster is more closely associated with the Mn atoms (Mn–O: 1.943, 1.956, 1.945 Å) than with the vanadiums (V–O: 2.394, 2.425, 2.429 Å). The latter values imply very low bond orders and favor a description in which V-1, V-2, and V-3 are five-coordinate.

In spite of their proximity to each other the manganese cations are remarkably magnetically dilute. Susceptibility measurements in the range 10–300 K reveal Curie–Weiss law behavior with $\theta = -2.9°$. The magnetic moment per manganese falls from 3.88 to 3.37 μ_B, and the temperature dependence of μ may be fitted to the expression for an exchange-coupled trimer of d^3 centers[26] with $J = -0.3$ cm^{-1}, see Figure 5. This behavior is in marked contrast to that of similarly constituted trimers of edge-shared MO_6 octahedra which generally feature strong metal–metal interactions.[27] The virtual absence of magnetic coupling observed in the present case is explained by the nature and size of the orbitals involved. The occupied 3d orbitals of Mn^{4+} are too small to allow direct metal–metal overlap (delocalization superexchange). Correlation superexchange involving 90° bridge angles is expected to be very weak when d^3 cations are involved.[28]

Acknowledgment. We thank Professor Ekk Sinn for the use of the magnetometer and T. Thanyasiri for susceptibility measurements. M.T.P. acknowledges the National Science Foundation for support.

Supplementary Material Available: Crystal structure reports, Tables IV and X (anisotropic thermal parameters), Tables V and XI (all bond distances and angles), and Figures 2 and 4 (unit cell contents projected along *c* and *a*, respectively) for $K_{10}Mn_2V_{22}O_{64}\cdot 20H_2O$ (**1**) and $K_5H_3Mn_3V_{12}O_{40}\cdot 8H_2O$ (**2**), respectively, and magnetic suceptibility data for **2** (36 pages); tables of observed and calculated structure factors for **1** and **2** (51 pages). Ordering information is given on any current masthead page.

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(26) Kambe, K. *J. Phys. Soc. Jpn.* **1950**, *5*, 48. The appropriate equation is

$$\mu_{Mn} = \left\{\frac{165 + 168x^9 + 105x^{15} + 40x^{21} + 2x^{24}}{5 + 8x^9 + 9x^{16} + 8x^{21} + 2x^{24}}\right\}^{1/2}$$

where $x = \exp(-J/kT)$.

(27) See, for example, the metal–metal bonded cations $M_3O_4(H_2O)_9{}^{4+}$, M = Mo(IV), W(IV) [Rodger, K. R.; Murmann, R. K.; Schlemper, E. O.; Shelton, M. E. *Inorg. Chem.* **1985**, *24*, 1313. Segawa, M.; Sasaki, Y. *J. Am. Chem. Soc.* **1985**, *107*, 5565].

(28) Goodenough, J. B. *Magnetism and the Chemical Bond*; Wiley Interscience: New York, 1963; p 180.